NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL-RUA

Regional University Alliance

NETL Carnegie Mellon PENNSTATE University of Pittsburgh VirginiaTech WestVirginiaUniversity URS

Electrode Engineering with Computational Leverage

Kirk Gerdes

DOE-NETL, Technical Coordinator – Fuel Cells

U.S. DEPARTMENT OF ENERGY

Acknowledgements

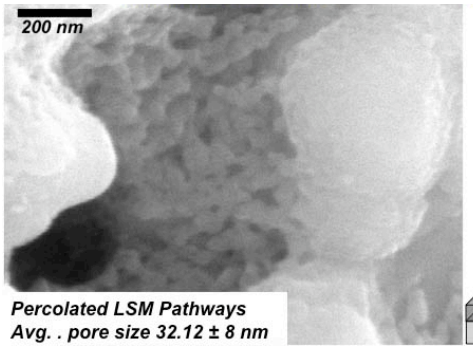
- **NETL RUA Fuel Cell Team**
  - Researchers at NETL, CMU, PSU, WVU, and URS
  - Bryan Morreale
- **SECA Program Management**
  - Briggs White, Joe Stoffa, and Rin Burke
  - Shailesh Vora and Dan Driscoll
- **NETL Multi-Media Team**
  - Michael Gipple
  - Bobby Snelson
  - Tim Ford

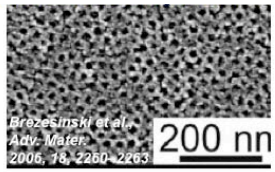
NETL RUA - Solid Oxide Fuel Cells

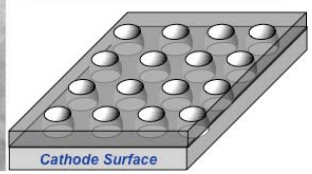
Support Industrial Development

Operation of NETL Solid Oxide Fuel Cell Multi-Cell Array on direct, coal-derived synthesis gas at the National Carbon Capture Center at Wilsonville, AL in August/Sept 2009.

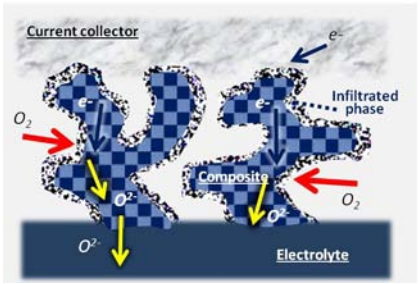
Collected 4,000 + cell-hours of data to support development of gas cleanup systems sufficient for gasifier / fuel cell integration.





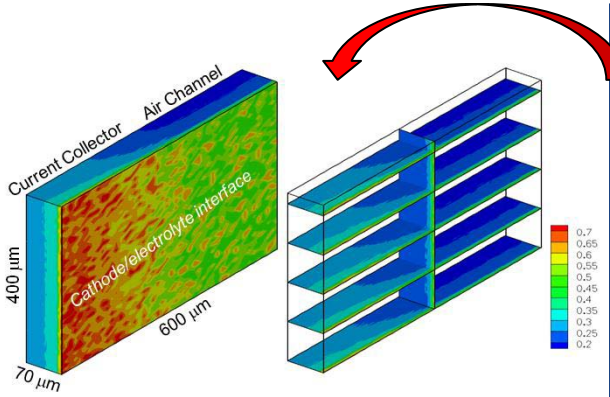


Innovate Technology



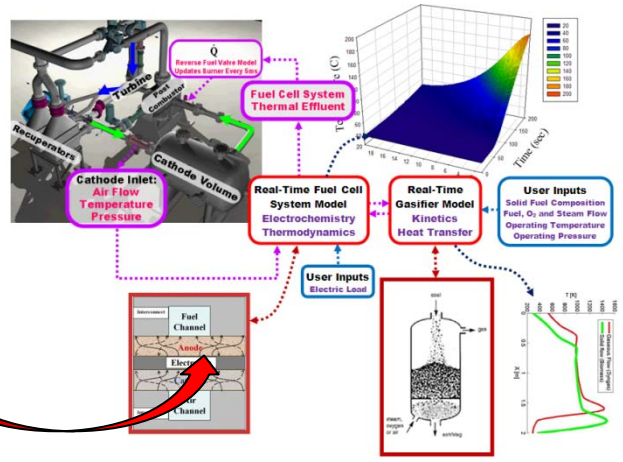
Cathode infiltration technology is being developed to enhance the SOFC operating performance. Initial results have demonstrated > 40% performance improvement and acceptable material stability.

Evaluate Advanced Concepts



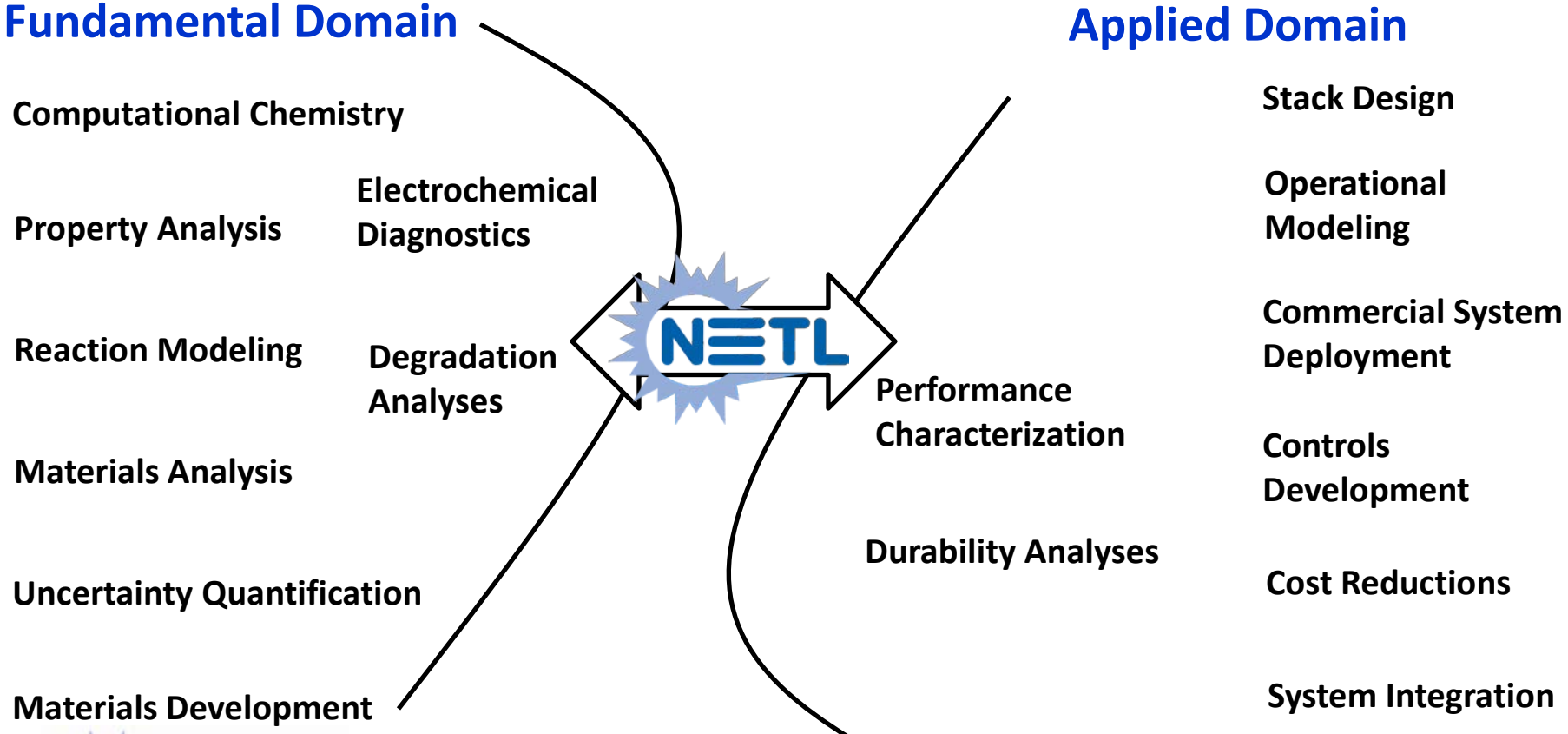
Fundamental computations (3D multi-physics model, at left) inform modeling of advanced degradation, performance, and microstructural evolution at the cell and stack level.

Integrated gasifier / fuel cell / turbine systems (IGFT, at right) support advanced fuel cell demonstrations efforts (2013+). NETL operates a system hardware evaluation and controls development platform.



NETL RUA Fuel Cells Team

Links fundamental examination and practical implementation



NETL RUA Fuel Cells Team

Electrode Engineering and Degradation Modeling

- Microstructural Evolution Model
- 3D Multi-physics Model
- Cell Degradation Modeling
- Oxygen Reduction Reaction Model
- 3D Reconstructions
- Microscopic/Spectroscopic Analyses
- Computational Chemistry
- Materials Development
- Electrode Engineering (Infiltration)
- Materials Development

3 Illustrations

- **Cathode Infiltration**
  Technology Scale-up and Transfer
- **Electrode Engineering**
  Stack Performance Control
- **Microstructural Evolution**
  Correlating structure and function

Cathode Infiltration

Primary contributors with posters at workshop

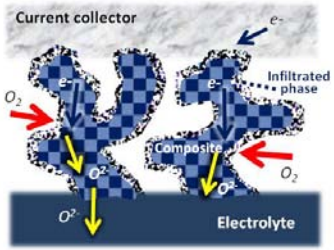
- **Shiwoo Lee** – National Research Council Senior Fellow, National Energy Technology Laboratory
- **Xueyan Song** – Asst Professor, Mechanical and Aerospace Engineering, West Virginia University
- **Yun Chen** – Research Asst Prof, Mechanical and Aerospace Engineering, West Virginia University

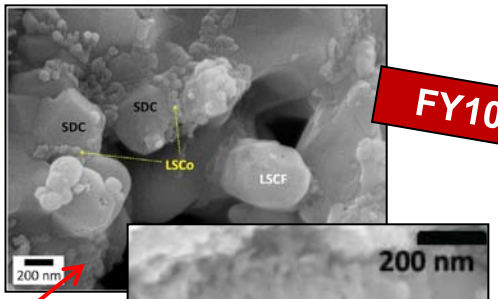
Additional contributors in NETL RUA infiltration research

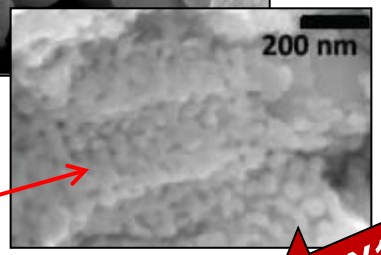
- **Ed Sabolsky** - Asst Professor, Mechanical and Aerospace Engineering, West Virginia University
- **Paul Salvador** – Professor, Materials Science and Engineering, Carnegie Mellon University

Cathode Infiltration

Infiltration concept



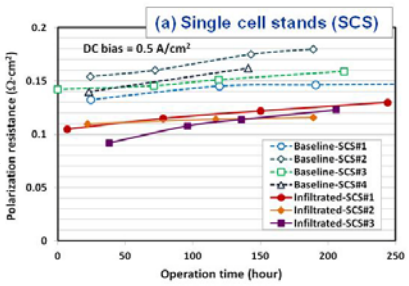


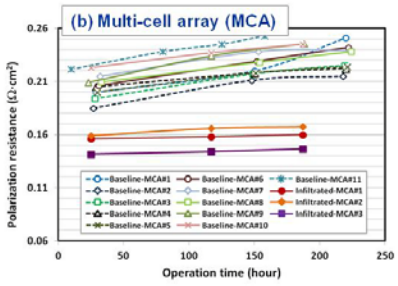


Cathode infiltrates
- **Nano-scale electrocatalysts**
- **High-surface area (EISA)**

FY10

➢ Polarization resistance vs. time of baseline cells and infiltrated cells





(a) Average Rp after 24 h operation (SCS)
Baseline cells: 0.14 ± 0.009 Ωcm²
Infiltrated cells: 0.10 ± 0.012 Ωcm²

(b) Average Rp after 24 h opeation (MCA)
Baseline cell = 0.21 ± 0.014 Ωcm²
Infiltrated cell = 0.15 ± 0.010 Ωcm²

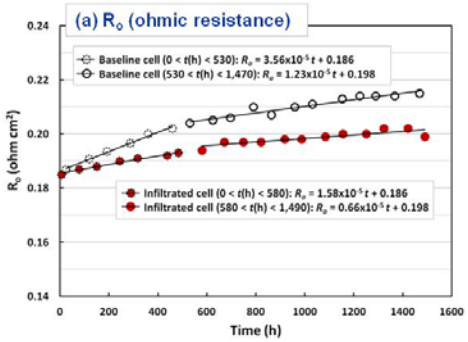
Short-term performance validation

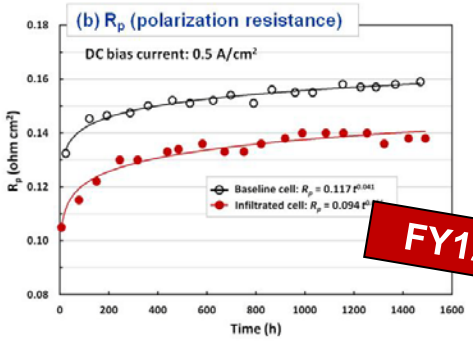
Demonstrated statistically significant performance improvement for infiltrated cathodes in 200 hour tests
> 30% peak power density increase (average) observed

FY11

Long-term stability verification

➢ Variation of R_o and R_p of selected baseline cell and infiltrated cell for 1,500 h



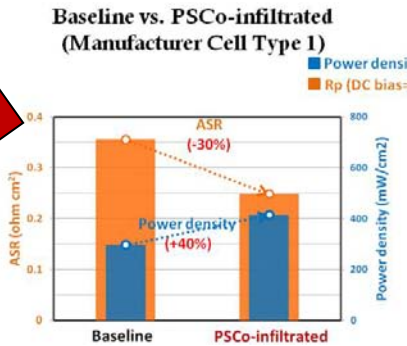


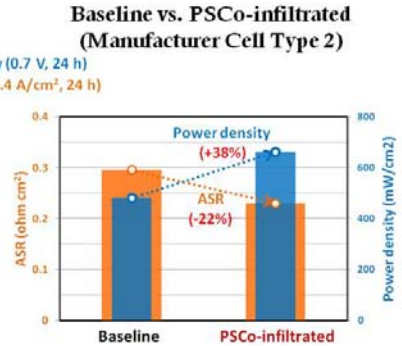
Verified stability of electrochemical performance in 1500 hour test, cell *degradation not accelerated* above baseline

FY12

Industry Engagement

Unaltered industry cells + unmodified infiltrate: 200 hour tests > 38% power density increase @ 0.7 V (average)





Images and data: Shiwoo Lee, National Energy Technology Laboratory
Paul Salvador, Carnegie Mellon University

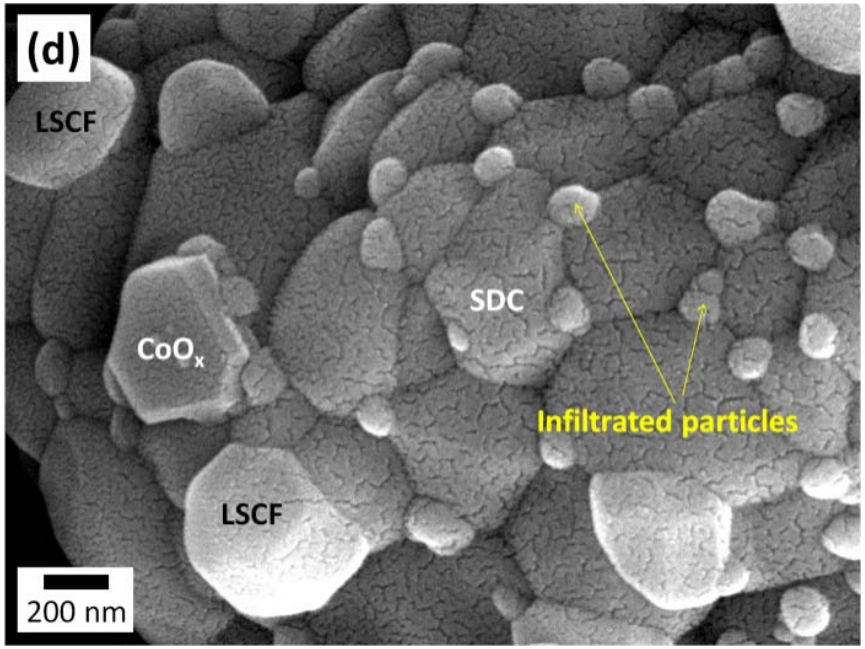
Cathode Infiltration

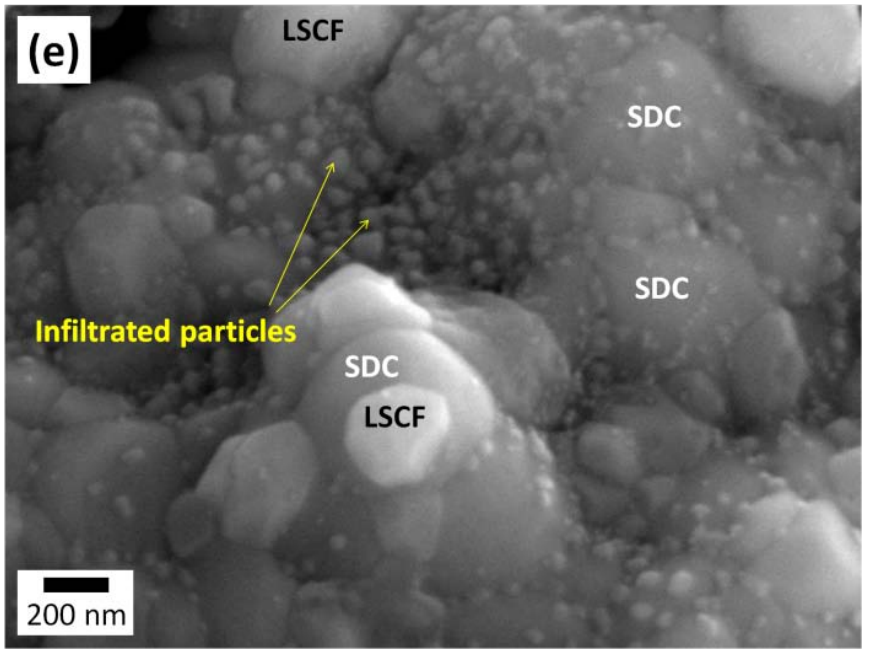
Topic: Effects of infiltration solution chemistry on microstructure

LSCoPt infiltration in SDC-LSCF cathode

❖ *Non-polymerization complex (NPC) route*

➢ Precursor solution composition: Nitrate of La, Sr, Co, and Pt
+ citric acid (**No ethylene glycol**)



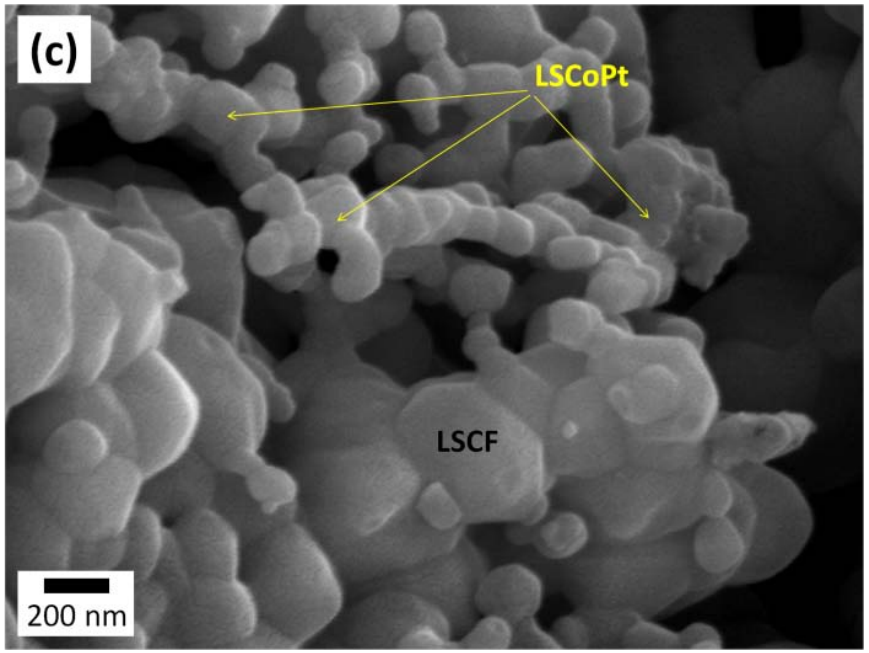


➢ Removal of ethylene glycol (non-polymerizable complexing process) made infiltrated particles much smaller in size (~ 50 nm) free of macro-network structure, even though high contact angle may be maintained.

Cathode Infiltration

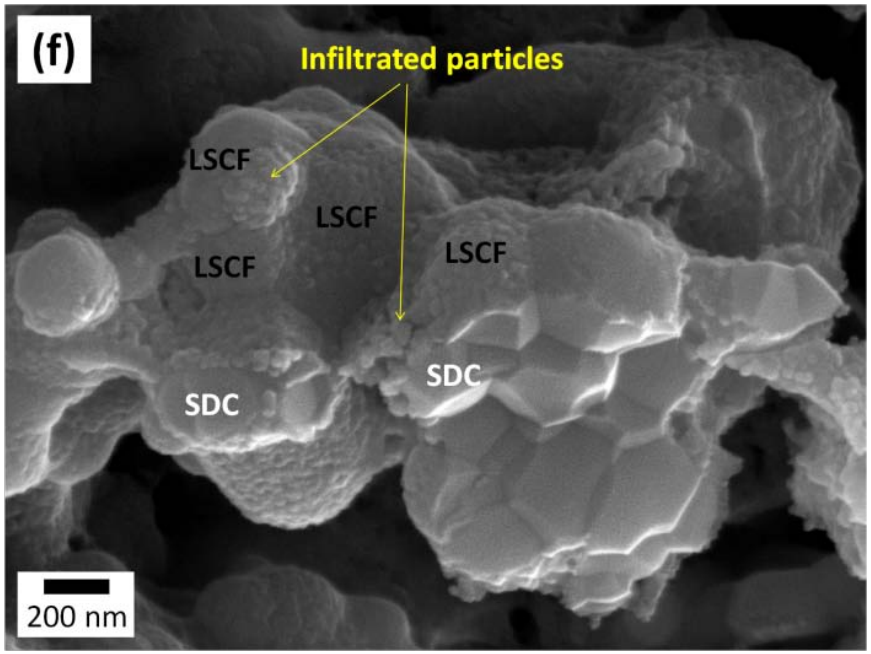
❖ *Non-Polymerization complex (NPC) route + mixed solvent*

Aqueous solvent



Mixed solvent

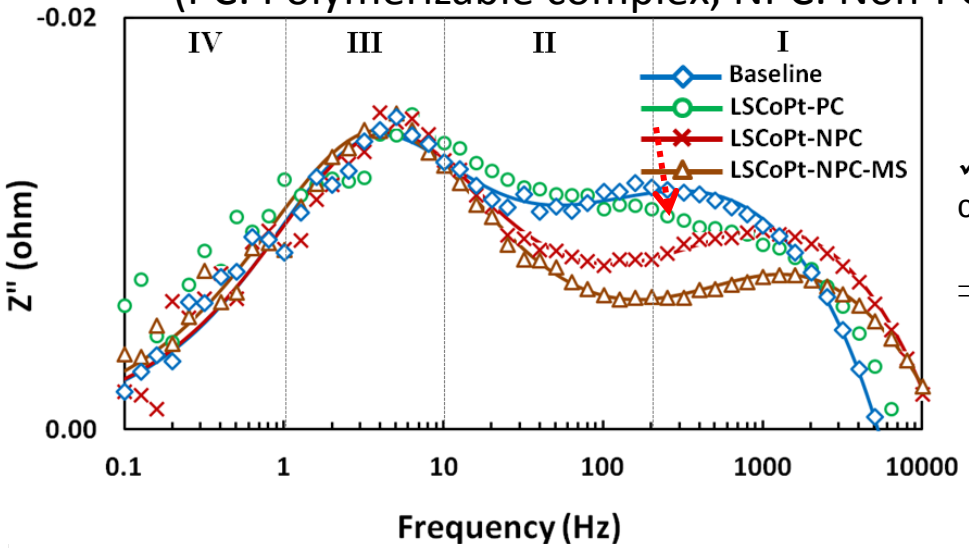
Azeotropic mixture of H_2O and EtOH



- Numerous fine infiltrate particulates are observed to coat surfaces of backbone grains homogeneously due to reduced surface tension of infiltration solution of mixed solvent.
- Ethanol (22.3 dyn/cm) and water (72.8 dyn/cm).

Cathode Infiltration

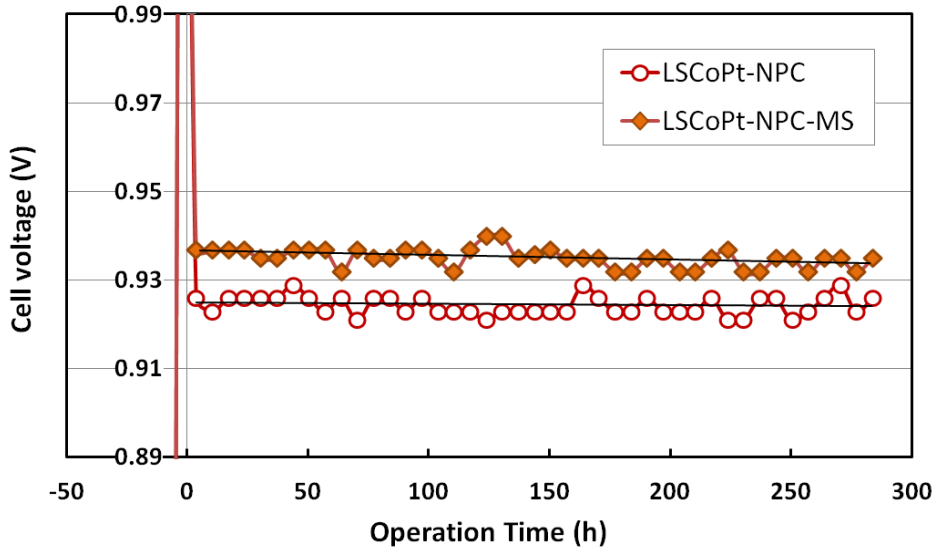
➢ **Bode plots of Baseline, LSCoPt-PC, LSCoPt-NPC, LSCoPt-NPC-MS**
(PC: Polymerizable complex, NPC: Non-PC, MS: Mixed solvent)



✓ Impedance of **region II (10-200 Hz) is reduced** for the cells LSCoPt-NPC and LCoPt-NPC-MS:

⇒ Evidence of **cathode activation by infiltration**

o Data were obtained under DC bias of 0.5 A/cm^2 after 24 h operation at 750°C. Solid lines are the data fitted to an equivalent circuit model.



➢ Cell voltage variation over 280 h under 0.25 A/cm^2

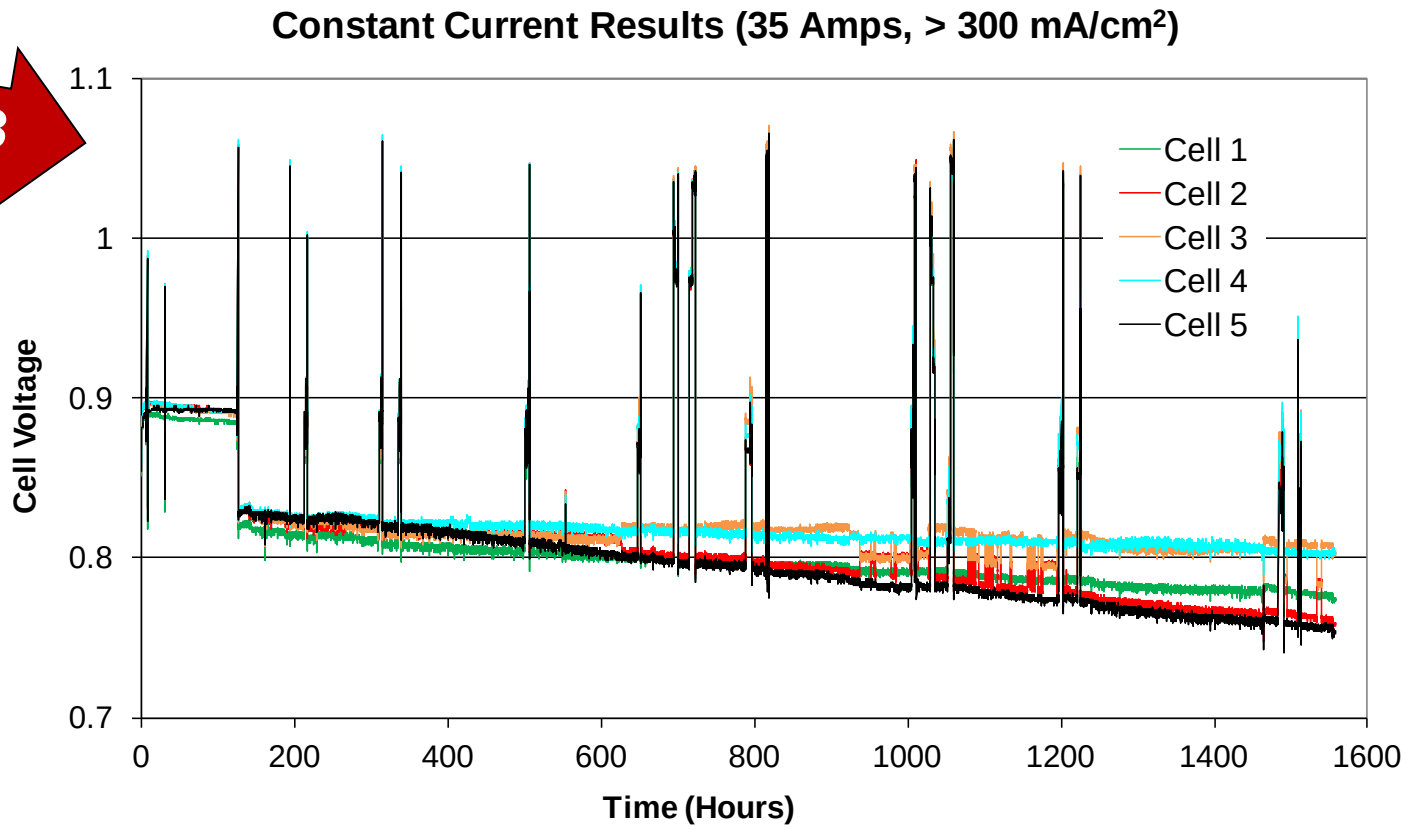
Linear slope of the cell voltage:

LSCoPt-NPC: **-0.39 10^{-2} mV/h (-0.42 %/1000h)**

LSCoPt-NPC-MS: **-1.20 10^{-2} mV/h (-1.28 %/1000h)**

Cathode Infiltration

FY13

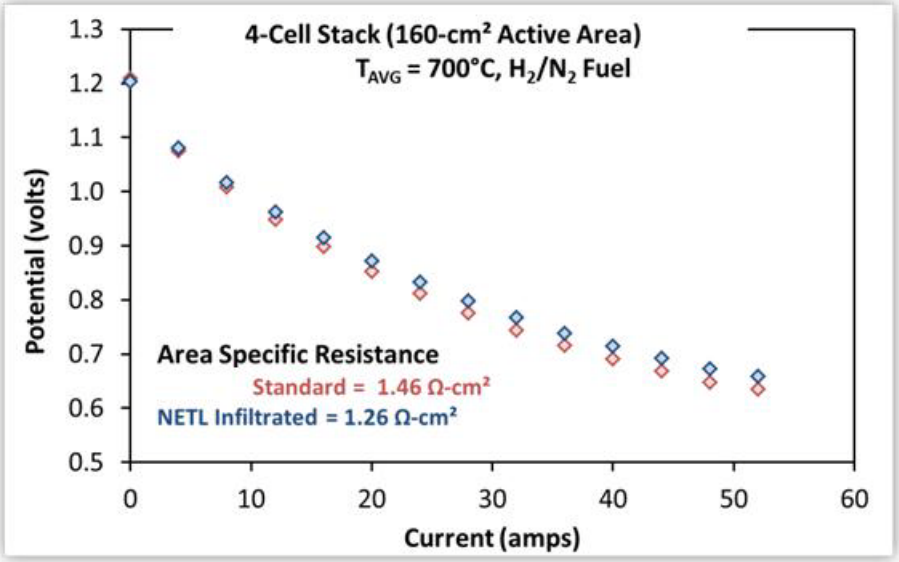


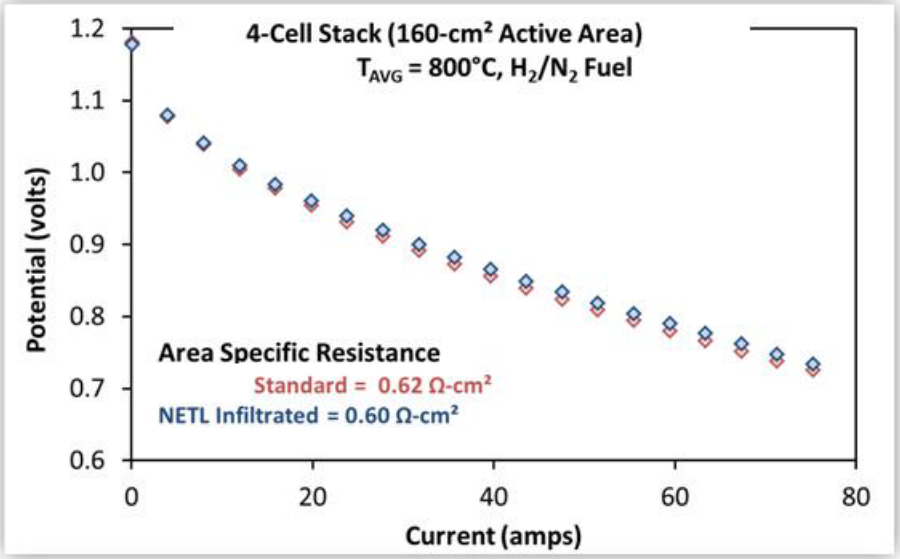
- Manufacturer 1 completed 1500+ hr short stack test of unmodified infiltrate material and conventional slip chemistry
- Repeating test with <u>customized infiltrate and slip chemistry</u>

Cathode Infiltration

FY13

- Manufacturer 2 performing on-going short stack test (> 500 hours) of unmodified infiltrate material / chemistry
- ASR @ 800°C improved by 3%
- ASR @ 700°C improved by 13%
- Plan to repeat test with <u>customized infiltrate</u>





Electrode Engineering

Potential applications of electrode engineering through infiltration are examined in a physically informed, simulated system

- **Ismail Celik** – Professor, Mechanical & Aerospace Engineering, West Virginia University
- **Raju Pakalapati** – Research Mechanical Engineer, West Virginia University
- **Xingbo Liu** – Associate Professor, Mechanical & Aerospace Engineering, West Virginia University
- **Hui Zhang** – Research Asst Prof, West Virginia University




- **Poster on this and related topics at session following**

Electrode Engineering

- Infiltration provides an additional tool to engineer active electrode interfaces
- Enables control over parameter distributions, both at cell-to-cell and localized scales
- Succinctly: Possible to depress state variable gradients within the SOFC stack
- Illustration: Control of cell overpotential distribution

Electrode Engineering

- **Simulation is created to examine the role of infiltrate in controlling overpotential**
- **Assumptions/Simulation Basis:**
  - Full cell multi-physics using ORR developed for LSM
  - Simulation baselined/calibrated for approximately 80 mV cathode overpotential at 800°C and 250 mA/cm^2 (cell average)
  - Infiltrate is modeled purely as increase in local activity of ORR
  - 3 cases are considered
    - Basecase (no infiltrate, with simulation output approximately matched to experiments)
    - Infiltrate uniformly applied to entire cathode
    - Infiltrate applied with 1D linear gradient parallel to gas flow
- **Simulation of local overpotential as a function of air utilization**
  - Assumes 15% as a standard value
  - Minimum of 10% utilization, maximum of 20% utilization

Electrode Engineering

- **Link to graphical representation here**

Electrode Engineering

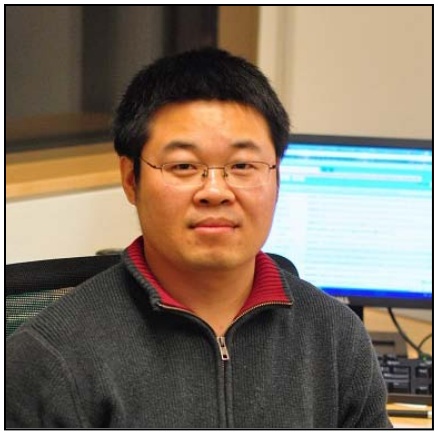
- **Results – Cathode overpotential difference from inlet to outlet**
  - Cathode overpotential gradient from inlet to outlet is controllable in cell

- **Implications**
  - Engineering the cathode overpotential (cathode activity) as a function of position inside the stack is possible.
  - *Infiltration provides a semi-independent technique for engineering stack performance and durability.*

Microstructural Evolution

Cathode aging and performance degradation attributable to microstructural evolution is examined

- **LongQing Chen – Professor, Materials Science & Engineering, Penn State University**
- **Linyun Liang – Post-Doctoral Scholar, Materials Science & Engineering, Penn State University**
- **Poster on this and related topics at session following**



Other contributors to this research

- **Shiwoo Lee – National Research Council Senior Fellow, National Energy Technology Laboratory**
- **Raju Pakalapati – Research Asst Prof, West Virginia University**
- **Paul Salvador – Professor, Materials Science and Engineering, Carnegie Mellon University**
- **Sudip Bhattacharya – Post-Doctoral Res Assoc, Materials Science & Eng, Carnegie Mellon Univ**

Microstructural Evolution

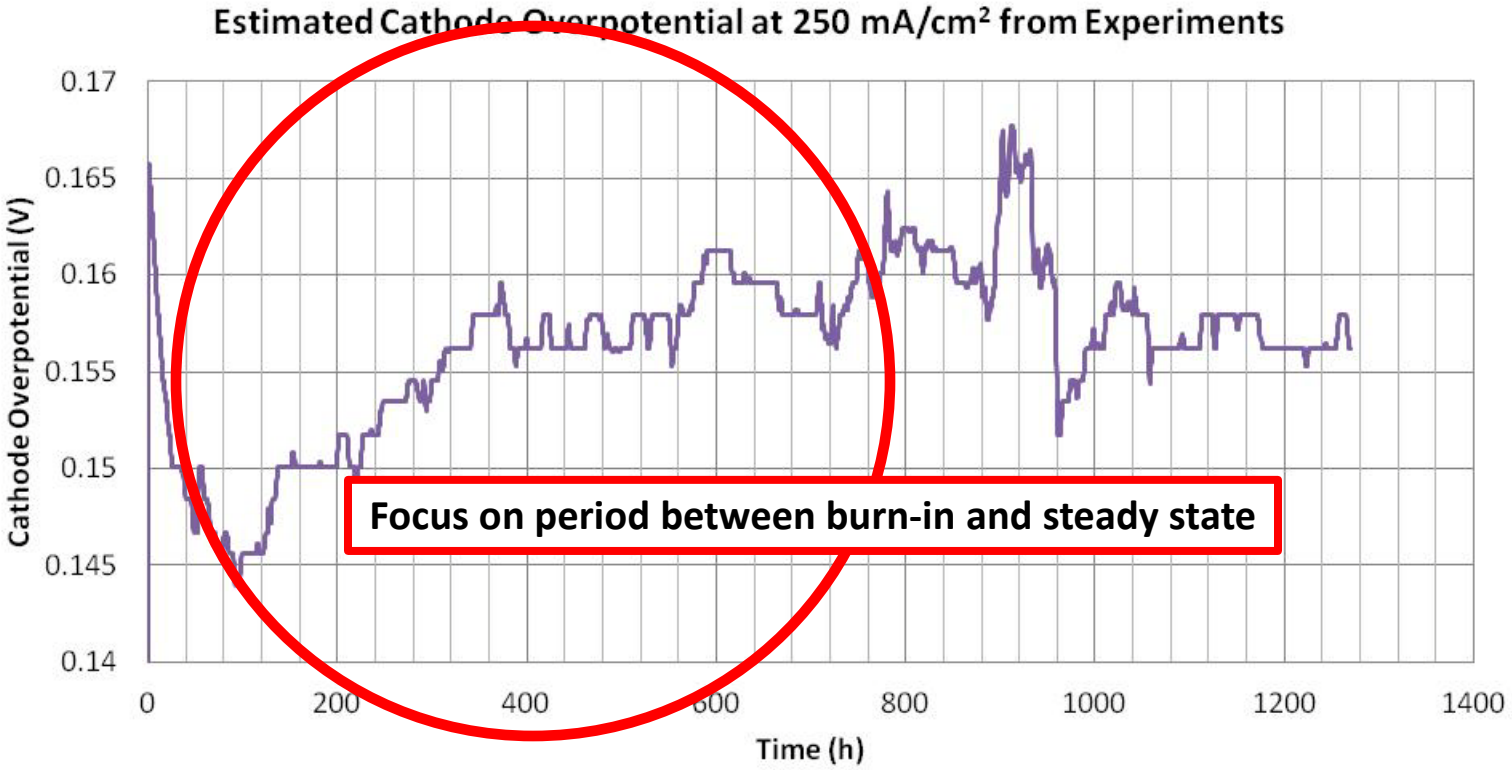
- Evolution of microstructure over long operating periods may be a significant source of long-term performance degradation
- Evolution manifests as coarsening of grains to diminish 3PB
- Also considers diffusion of cations and generation of secondary phases

Microstructural Evolution

- **Simulation is created to examine the role of microstructural coarsening on overpotential in operated SOFC**
- **2 possible routes to calibrate/tune model:**
  - BEST: Measure surface energies of aged specimen
  - NEXT BEST: Tune model parameters to match aged specimen
- **Assumptions and simulation basis for present model:**
  - Measured cell overpotential is exclusively the result of cathode coarsening
  - 3PB length is calculable using 3D multi-physics model and measured cell overpotential (lower than conventional 3PB concentration is used)
  - 2 cases are considered
    - Measured overpotential change is 100% attributable to 3PB degradation
    - Measured overpotential change is 50% attributable to 3PB degradation
- **Correlate cell average overpotential as a function of 3PB length**

Microstructural Evolution

Experimental Data

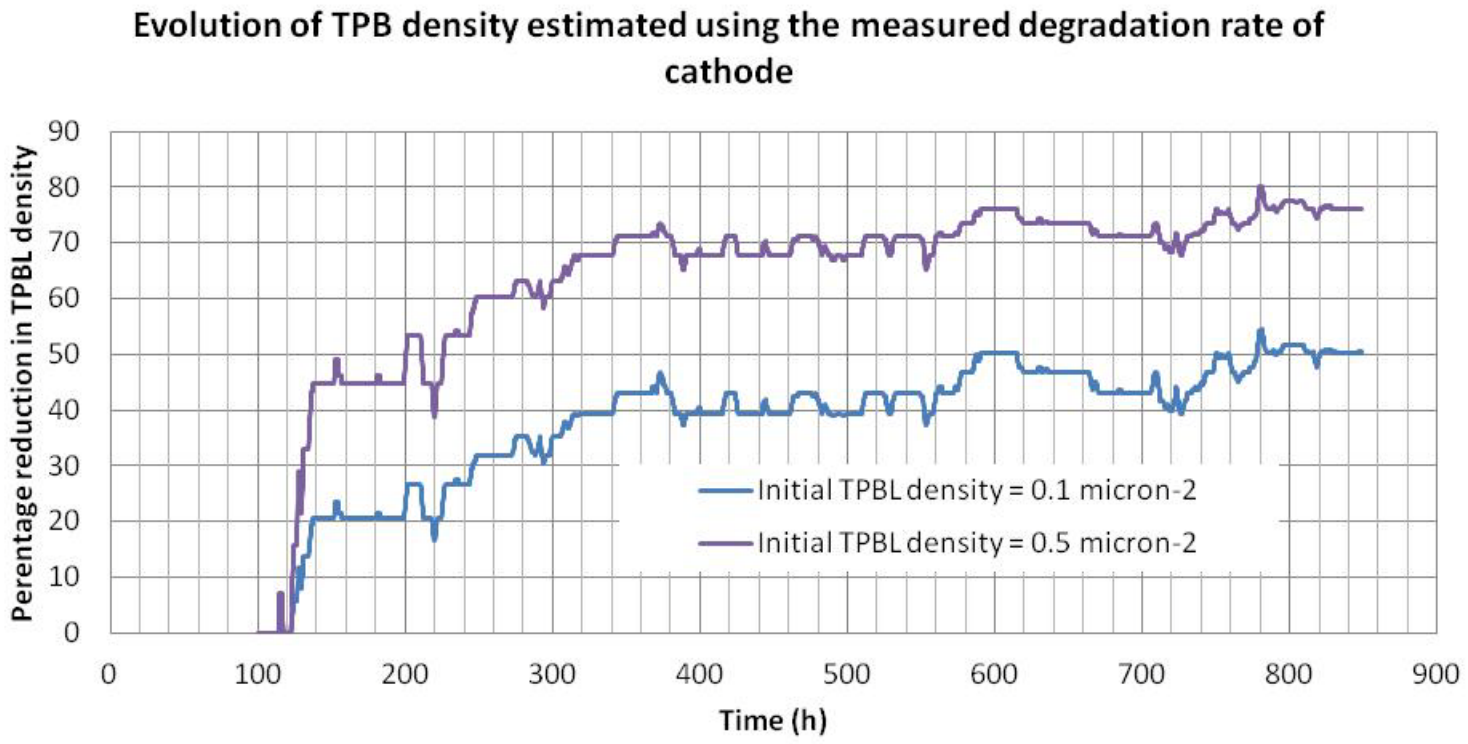


The discontinuities are removed and the data are smoothed over 2 hour intervals

Data: Shiwoo Lee, NETL
Figure: Raju Pakalapati, WVU

Microstructural Evolution

Multi-Physics Simulation



Analysis and Figure: Ismail Celik and Raju Pakalapati, WVU

Microstructural Evolution

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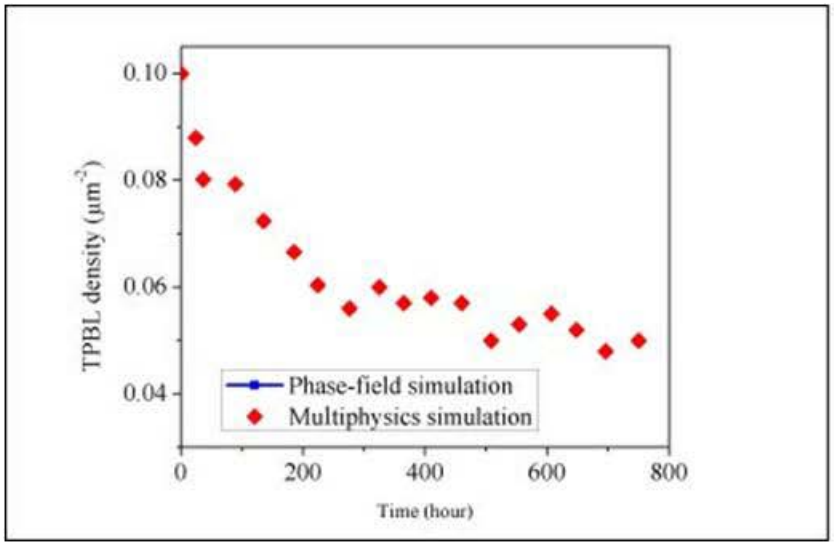

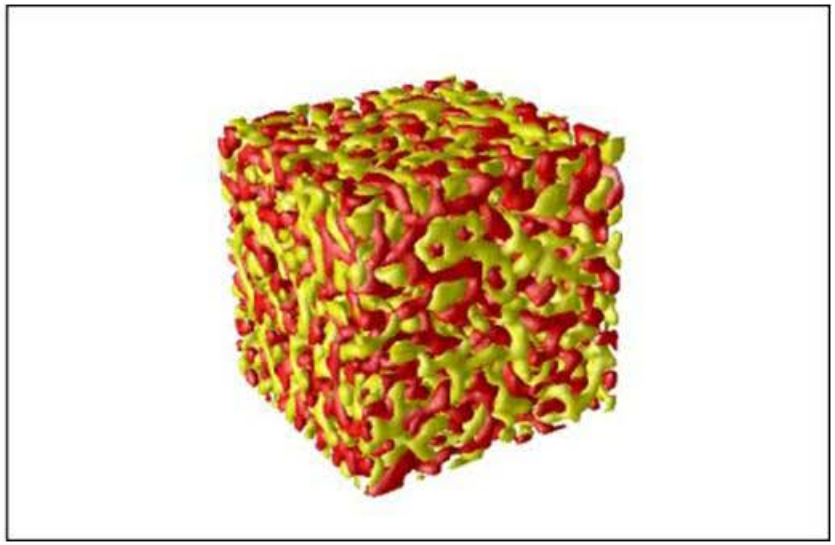

100% of measured degradation occurring in first 750 hours of operation is attributable to cathode coarsening

Analysis and Figures: LongQing Chen, Linyun Liang, PSU

Microstructural Evolution

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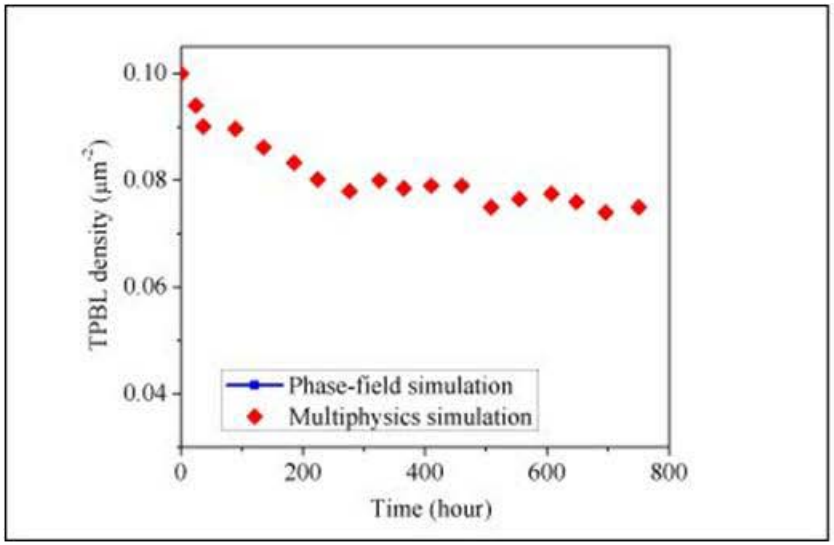

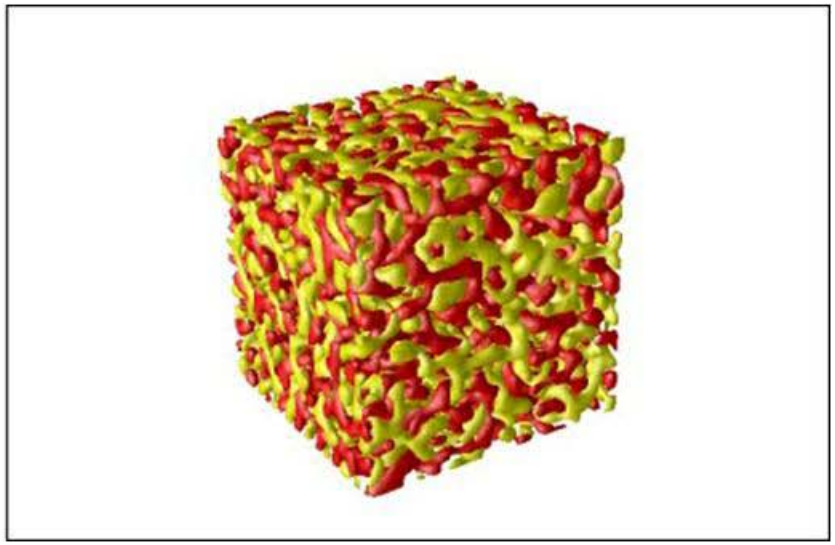

50% of measured degradation occurring in first 750 hours of operation is attributable to cathode coarsening

Analysis and Figures: LongQing Chen, Linyun Liang, PSU

Summary

3 illustrations describe collation of fundamental, discrete research activity leveraged for industrial purposes

Illustrations convey possibility of detailed engineering and development using simulations grounded in physics

NETL priority: Pursue collaborative development focused on specific (industry relevant) materials and microstructures

Ideal pursuit: Model development and engineering with strong industry guidance and highest possible magnitude of collaboration

Final Acknowledgements

Poster on the topic of cation segregation (cathode deactivation)

- **Harry Finklea** – Professor, Chemistry, West Virginia University
- **Harry Abernathy** – Research Materials Scientist (photo not included)

Business development activity

- **Tom Kalapos** – Fuel Cells Activity Manager, URS Corp (NETL)